



Oxidation of organic substrates catalyzed by a novel mixed-ligand ruthenium(III) complex

Debabrata Chatterjee^{a,*}, Anannya Mitra^a, B.C. Roy^b

^a Chemistry Section, Central Mechanical Engineering Research Institute, Durgapur — 713209, India

^b Chemistry Section, Jadavpur University, Calcutta — 700032, India

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Abstract

Cationic $[\text{Ru}^{\text{III}}(\text{app})(\text{bipy})(\text{H}_2\text{O})]^{2+}$ (**1**) complex ($\text{H}_2\text{app} = N$ -(hydroxyphenyl)pyridine-2-carboxaldimine; bipy = 2,2'-bipyridyl) has been synthesized and characterized by physico-chemical methods. Complex **1** is found to be an effective catalyst in the oxidation of both saturated and unsaturated hydrocarbons by using *tert*-butylhydroperoxide (*t*-BuOOH). A mechanism involving formation of and transfer from a reactive high valent Ru(V)-oxo species as catalytic intermediate is proposed for the catalytic processes. The results of the product distribution in the present investigation clearly indicate the preference for side-on approach of olefins and the high electrophilic nature of Ru=O bond in $[\text{Ru}^{\text{V}}(\text{app})(\text{bipy})\text{O}]^{2+}$ intermediate complex, which leads to the higher affinity of hydrogen atom/hydride abstraction than oxo-transfer to C=C double bond. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal catalyzed oxo-functionalization of hydrocarbons is a subject of fundamental and technological importance [1–5]. In this regard, metalloporphyrins have been used [6] extensively, owing to their direct relationship to enzymatic oxidation with cytochrome P-450 [7–9]. The same catalytic oxidation reactions are mimicked by various transition metal complexes [10–23] containing non-porphyrinic ligands, viz. Schiff-bases, polypyridyl ligands, etc. In this regard, ruthenium complexes by virtue of their

wide range of reversible and accessible oxidation states have proved to be useful catalysts for oxidation of organic substrates using molecular oxygen [18,19], iodosylbenzene [24,25], hypochlorite [26–29], oxone [30] and *t*-butylhydroperoxide [31–33]. Use of alkyl hydroperoxide is of particular interest in view of its ability towards oxo-functionalisation of aliphatic C–H bond, selectively in presence of ruthenium catalyst complexes. Safety and environmental concerns have attached special importance to the catalytic scheme with alkyl hydroperoxides and hydrogen peroxide. Our current research, interest [34–38] is focused on the studies of oxygenation of saturated and unsaturated hydrocarbons catalyzed by transition metal complexes of non-porphyrinic ligands. Evaluation of metal complexes with the requisites necessary for effective and selective catalytic

* Corresponding author. Tel.: +91-343-546818; fax: +91-343-546745.

E-mail address: root@cscmeri.ren.nic.in (D. Chatterjeea).

transformation is our goal. We have thus undertaken an investigation of hydrocarbon oxidation with *tert*-butylhydroperoxide (*t*-BuOOH) catalyzed by a new $[\text{Ru}^{\text{III}}(\text{app})(\text{bipy})(\text{H}_2\text{O})]^{2+}$ ($\text{H}_2\text{app} = N$ -(hydroxyphenyl)pyridine-2-carboxaldimine; bipy = bipyridyl) complex (**1**). The present paper reports the synthesis and characterization of complex **1**, along with its reactivity towards oxidation of organic substrates in presence of *t*-BuOOH.

2. Experimental

2.1. Materials

1 was synthesized by interacting RuCl_3 with 2-pyridine carboxaldehyde, 2-aminophenol and 2,2'-bipyridyl (bipy) in a stoichiometric ratio. To a methanolic solution (15 ml) of 2-aminophenol (0.218 g, 2 mmol), 2-pyridine carboxaldehyde (0.214 g, 2 mmol) was added and stirred for 30 min. Upon addition of RuCl_3 , $3\text{H}_2\text{O}$ (0.522 g, 2 mmol) to this solution, the yellow colour changed to dark brown. After being refluxed for 2 h, 2,2'-bipyridyl (0.312 g, 2 mmol) was added and the reaction mixture was further refluxed for 6 h. The dark brown solution, which upon evaporation to dryness yielded a solid, was washed thoroughly with water–methanol (8:2) mixture, and finally, dried in desiccator over CaCl_2 . Yield (82%). Anal. Calculated for $\text{RuC}_{22}\text{N}_4\text{O}_3\text{H}_{21}\text{Cl}_2$: C, 47.06; H, 3.74; N, 9.98. Found: C, 47.12; H, 3.49; N, 10.13. UV–Vis data in CH_3CN (λ_{max} , nm (ϵ_{max} , $\text{M}^{-1}\text{cm}^{-1}$): 242 (7062), 475 s (4266), 550 (4030). IR (cm^{-1}): 1580, 1240. $\mu_{\text{eff}} = 1.98$ BM. All other chemicals and solvents were of A.R. grade and used as obtained. Doubly-distilled water was used throughout the experiments.

2.2. Instrumentation

The electronic absorption spectra were measured with a GBC Cintra 10 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer (Model 783) spectrometer (using KBr pellets). Electrochemical studies were carried out in acetonitrile medium by using tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte. A PAR Electrochemical equipment (Model 174A), equipped with a platinum working electrode, and a standard calomel electrode

(SCE) as reference were used for this purpose. All potentials are expressed against SCE. Magnetic susceptibility was measured by using a PAR-155 vibrating sample magnetometer. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N).

2.3. Procedure of catalytic studies

In a typical experiment, 0.1 mmol of complex **1**, 0.1 mmol of benzyltributylammoniumchloride (phase transfer catalyst, PTC) and 10.0 mmol of substrate in 10 ml of CH_2Cl_2 were magnetically stirred with 10.0 mmol *t*-BuOOH (70% aqueous solution) at room temperature. Aliquots of the CH_2Cl_2 layer was withdrawn at chosen interval of time subjected to gas chromatographic (GC) analysis for product(s). Gas chromatographic analyses were performed with a Carlo Erba GC 8000^{Top} series on a Tenax column connected with a FID detector. GC parameters were quantified by the authentic product samples prior to the analysis.

3. Results and discussion

The structural representation (tentative) of the complex **1** is shown in Fig. 1. The IR spectrum of the complex **1** shows bands at 1580 and 1240 cm^{-1} , corresponding to coordinated C=N– and C–O–stretchings. The UV–Vis spectrum of complex **1** in CH_3CN (Fig. 2) is characterized by charge transfer bands. The bands appear before 300 nm are characterized by intra-ligand charge transition, whereas, bands displayed in the visible region are assigned to the ligand to metal charge transfer bands (relating to $\pi \rightarrow t_{2g}$ (Ru) transitions. The basis of assignment is the earlier reports [39,40] on the spectral data (in CH_3CN) for a group of mixed-ligand complexes of ruthenium(III) containing bipy and L (where L = tertiary phosphines, chelating phosphines, isonitrosoketones) [39,40]. These complexes showed one or more ligand to metal charge transfer (l.m.c.t.) bands ($\pi \rightarrow t_{2g}$ origin) in the visible region. Complex **1** was electrochemically examined at a platinum-working electrode in acetonitrile solution. Cyclic voltammogram of complex **1** showed one quasi-reversible couple at $E_{1/2} = 0.54$ V (vs. Ag/AgCl) with a peak-to-peak separation (ΔE_p)

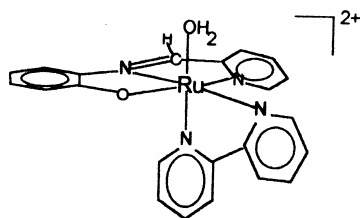


Fig. 1. Schematic representation of complex-1.

value of 120 mV. This couple is assigned as $[\text{Ru}^{\text{III}}(\text{app})(\text{bipy})\text{H}_2\text{O}]^{2+} - [\text{Ru}^{\text{II}}(\text{app})(\text{bipy})\text{H}_2\text{O}]^+$ redox couple. Constant-potential coulometry and current height consideration confirmed the one-electron nature of the redox process ($n = 0.98$; $i_{\text{pa}}/i_{\text{pc}} \sim 1$).

Spectral changes that occurs by addition of *t*-BuOOH to an aqueous solution of complex **1** is shown in Fig. 2. The appearance of the peak at 392 nm is attributed to the formation of high-valent Ru(V)-oxo species by considering the close resemblance of the spectral features of oxo-ruthenium(V) complexes reported earlier [17,18,28,41–44]. Further, support in favour of the formation of oxo-ruthenium(V) species came from the IR spectrum of the solid mass (obtained by evaporation of the resultant solution to dryness), which showed a band at 860 cm^{-1} , characteristic of ruthenium(V)-oxo species [17,18,28,41–44].

Catalytic oxidations of the organic substrates (*S*) was carried out in a biphasic medium ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$) in the presence of a PTC benzyl-

tributylammonium chloride. The results of the complex **1** catalyzed reaction (see Section 2 for reaction conditions) are summarized in Table 1. Blank experiments established that each component is essential for an effective catalytic transformation and the oxidation did not take place under O_2 in absence of *t*-BuOOH. Complex **1**/*t*-BuOOH system does not epoxidise cyclohexene, but rather, hydroxylates to cyclohexene-1-ol. In the earlier reports [32,33] on Ru(III)-complexes catalyzed conversion of cyclohexene to cyclohexene-1-ol using *t*-BuOOH, formation of a Ru(V)-oxo intermediate was proposed. Results of the present investigation once again suggests that the source of oxygen transferred in the formation of cyclohexene-1-ol from cyclohexene is a Ru(V)-oxo complex. Approach of the allylic hydrogen (filled σ orbital of $\alpha\text{-C-H}$) of cyclohexene seems to be kinetically favoured than that of the olefinic unit (i.e. π -filled MO of olefin) towards highly electrophilic $\text{Ru}=\text{O}$ bond. The special affinity of $[\text{Ru}^{\text{V}}(\text{app})(\text{bipy})\text{O}]^{2+}$ for oxo-functionalisation of C–H bond may be explicable, at least conceptually, in terms of free access of allylic C–H bond (to the $\text{Ru}=\text{O}$ bond) through side on approach [45], as the coordinated ‘app’ ligand is flat (Fig. 3). There was no epoxide obtained using other terminal oxidants like KHSO_5 , NaOCl and H_2O_2 , and formation of cyclohexene-1-ol in each case suggests the generation of Ru(V)-oxo complex as an active intermediate in the formation of cyclohexene-1-ol. With stilbenes, oxidative cleavage of the C=C double bond to yield benzaldehyde appears to be the dominant reaction,

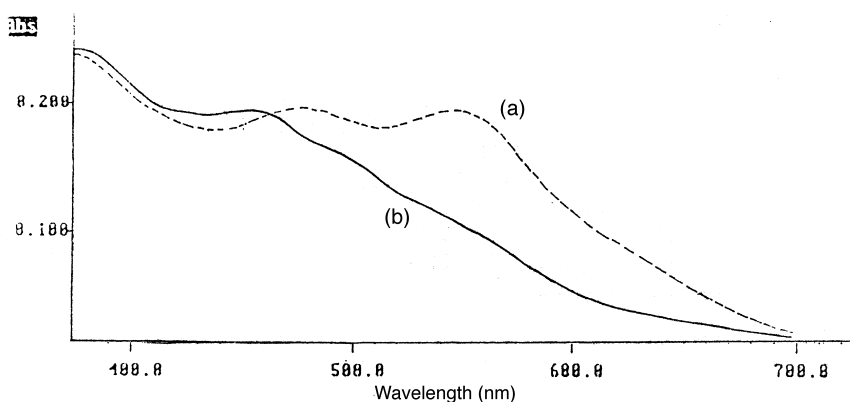


Fig. 2. Spectra of (a) complex-1 and (b) complex-1 + *t*-BuOOH (spectra taken after 90 mins of mixing), $[\text{complex-1}] = 1.34 \times 10^{-4}\text{ M}$, $[\text{t-BuOOH}] = 2 \times 10^{-3}\text{ M}$, pH = 5.0 (acetate-buffer), $T = 25^\circ\text{C}$.

though epoxides are also produced in the reaction mixture (Table 1). In order to know the decline in yield of the epoxide products, oxidation of *cis*- and *trans*-stilbene epoxides was examined with complex **1**/*t*-BuOOH system and it was found that benzaldehyde is the reaction product in both cases, but in low yield. This suggests that the pathway involved in benzaldehyde formation does not require prior formation of either *cis*- or *trans*-stilbene oxide. The formation of epoxides in case of stilbene oxidation (though in poor yields) are explicable with regards to the fact that it must add an oxygen atom to preserve the coordination number 4 at carbon. More important aspect of the present catalytic system is that the complex **1**, in the presence of *t*-BuOOH, can readily functionalise C–H bond of various organic substrates. It is capable of oxidising cyclohexane to cyclohexanol, toluene to benzyl alcohol and tetrahydrofuran to γ -butyrolactone. For alcohols, it oxidises cyclohexanol to cyclohexanone and benzyl alcohol to benzaldehyde. Complex **1**/*t*-BuOOH system could not oxidise *t*-BuOH. This supports the need for an α -hydrogen adjacent to the hydroxyl group for hydride transfer. The relatively higher product yield obtained for oxidation of benzyl alcohol than cyclo-

Table 1

Results of the complex **1** catalysed oxidation of organic substrates with *t*-BuOOH^a

Substrate	Product(s) ^b	Yield (%) ^c
Cyclohexene	Cyclohexene-1-ol	60
	Cyclohexene-1-one	5
Cyclohexane	Cyclohexanol	4
	Cyclohexanone	10
Cyclohexanol	Cyclohexanone	27
	Benzaldehyde	80
<i>cis</i> -Stilbene	<i>cis</i> -Stilbeneoxide	3
	<i>trans</i> -Stilbeneoxide	7
<i>trans</i> -Stilbene	Benzaldehyde	77
	<i>cis</i> -Stilbeneoxide	2
	<i>trans</i> -Stilbeneoxide	6
<i>cis</i> -Stilbeneoxide	Benzaldehyde	25
<i>trans</i> -Stilbeneoxide	Benzaldehyde	27
Tetrahydrofuran	γ -Butyrolactone	43
Toluene	Benzylalcohol	5
	Benzaldehyde	23
Benzylalcohol	Benzaldehyde	45

^aSee Section 2 for reaction condition.

^bAfter 4 h of reaction.

^cBased on substrate concentration.

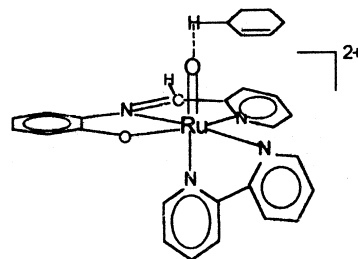


Fig. 3. Side-on attack of the C–H bond of cyclohexene on Ru(V)-oxo intermediate.

hexanol (Table 1) is due to the fact that α -CH unit of benzyl alcohol is more acidic than cyclohexanol. If a transfer of OH^- is important to assist hydride transfer, the better H-bonding hydroxyl donor (benzyl alcohol) would have an advantage kinetically. Thus, the results of alcohol oxidation (Table 1) in the present case are consistent to the orthogonal α -CH approach advocated by Cundary and Drago [45].

4. Conclusion

A new ruthenium complex, **1**, is synthesized. The results of the present studies convincingly demonstrate the catalytic ability of the reported complex (**1**) for oxo-functionalisation of aliphatic C–H bond with *t*-BuOOH. A high-valent Ru(V)-oxo complex is proposed to be the active species in the catalytic process. The presence of ‘bipy’ (which makes the oxo group enough electrophilic in nature) and flat ‘app⁻’ (which fulfills the steric requirement for free approach of C–H bond orthogonal to Ru=O bond) probably leads the reported catalytic system to the preferential C–H bond functionalisation via hydrogen atom/hydride abstraction.

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